Polarographic Behavior of Metal Acetylacetonates in Acetylacetone as New Non-Aqueous Electrochemical Medium

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The purification method of acetylacetone has been developed for a new electrochemical non-aqueous solvent, and some physical and chemical properties of acetylacetone have been characterized. The specific conductivity is 2.6×10^{-8} mho/cm, and the accessible potential range at the dropping mercury electrode is from -0.2 to -2.25 V *vs.* Ag/0.1 *M* $AgClO_4$ in the pure solvent containing 0.1 *M* TBAP. The solubilities of $LiClO_4$, $NaClO_4$, and Bu_4NClO_4 are more than 1 *M*, and these salts can be used as supporting electrolytes. The polarographic reduction behavior of metal acetylacetonates such as Mn(III), Co(III), Fe(III), Pb(II), Cu(II), Ni(II), and U(VI) were studied by DC, Tast DC, Pulse, Differential pulse, AC, and Phase sensitive AC polarographies. The effect of the concentration of the supporting electrolyte Bu_4NClO_4 on the polarographic reductions of metal acetylacetonates were also examined.

KEY WORDS: Acetylacetone / Metal acetylacetonate / Non-aqueous polarography / Purification of acetylacetone / Physical properties of acetylacetone /

INTRODUCTION

Acetylacetone (AA) is a dipolar protogenic solvent which has been widely used both as a chelating reagent and an extracting solvent in the spectrophotometric determination of metal ions.[1] Acetylacetone, however, has been not fully used as a non-aqueous solvent, particularly in the polarographic study of metal ions, because purification method effective enough for the electrochemical measurements has not been developed.

This communication deals with the purification method of acetylacetone for the electrochemical use, some physical and chemical properties of the solvent, and the polarographic behavior of metal acetylacetonates in the solvent.

EXPERIMENTAL

Purification of Solvent

Although some methods have been proposed[2~4] for the purification of acetylacetone as the extracting solvent and/or chelating reagent for spectrophotometry, they were found not to be satisfactory for the polarographic purposes. In the present study, the purification procedures have been developed as follows[5];

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Method A. *Step 1:* reflux over sodium bicarbonate (20 g per liter of analytical grade AA) for half an hour then distil at 48±5°C under reduced pressure (20~30 mmHg) through a column packed with helices.
Step 2: reflux over phosphorus pentoxide (10 g per liter of AA) and carry out fractional distillation under reduced pressure, using a high reflux-ratio column packed with helices. This method gave about 60% yield of the solvent having a specific conductivity of 2.6×10^{-8} mho/cm, which is effective enough for the non-aqueous polarographic studies.

Method B. *Step 1:* strip out the metals contained in the recovered AA into an aqueous phase using 100 ml of 0.1 *M* sulfuric acid per liter of AA.
Step 2: add sodium bicarbonate till the pH of organic phase becomes 4.0 then distil by Step 1 of method A.
Step 3: follow both steps of Method A. After a single use in the experiment, acetylacetone is recovered by this method.

For the extraction polarography, the solvent can be purified sufficiently by either Step 1 of Method A or Steps 1 and 2 or Method B.

Reagents

Tetrabutylammonium perchlorate (TBAP) and other tetraalkylammonium salts were prepared and purified according to the procedures recommended by one of the authors (T. F.).[6] Acetylacetonates of uranyl (VI)[7] and iron (III)[8,9] were prepared by extracting the corresponding chelates into benzene from the ammonical aqueous solution of metal nitrates, and recrystallized from hot benzene three times. Lead (II) acetylacetonate was prepared according to the procedure of Krishen and Freiser,[7] and used without further purification because this chelate was found not to be stable enough and the composition seemed not to be a simple form of $PbAA_2$. The other metal acetylacetonates were obtained from Dojin Chemicals and recrystallized from 95% alcohol.[2,8,9] All compounds were dried at 70°C under reduced pressure before use. The other chemicals used were of analytical reagent grade.

Apparatus

A Princeton Applied Research (PAR) Polarographic Analyzer, Model 174, was used for the measurements of conventional DC (DC), current-sampled DC (SDC), pulse (P) and differential pulse (DP) polarograms. PAR Differential Preamplifier; Model 117, Lock-in Amplifier; Model 124, and AC Polarographic Analyzer Interface; Accessory 174/50, were used to measure current-sampled AC (AC) and Tast phase sensitive AC (PSAC) polarograms. These polarograms were recorded at the sweep rate of 2 or 5 mV/sec with a National X-Y Recorder, Model VP-6431A.

The dropping mercury electrode (DME) was connected with a PAR Drop Timer Assy; Accessory 174/70. The DME used had the following characteristics in open circuit with 50 cm head of mercury in 0.1 *M* TBAP – AA solution: m=1.22 mg/sec and t=2.80 sec (natural drop time), and m=1.22 mg/sec and t=2.01 sec (controlled drop time). A spiral platinum wire was used as the counter electrode. A silver – silver perchlorate electrode in AA was used as the reference electrode [Ag/0.1 *M* $AgClO_4$ (AA)]. The potential of this reference electrode was +0.783 V

vs. aq. SCE and +0.882 V *vs.* mercury pool in 0.1 *M* TBAP–AA solution. The polarographic cell used was a conventional H-type one with a fine porosity sintered glass disc between the two compartments. The electrolysis solution were thoroughly deaerated by bubbling nitrogen gas for 10~20 minutes through the series of the columns of silica gel-phosphorus pentoxide-silica gel and the solvent.[10] All measurements were carried out at 25±0.1°C.

RESULTS AND DISCUSSION

Physical and Chemical Properties of Acetylacetone

The physical and chemical properties of AA are summarized in Table I. In addition to being mixed with ethanol and diethyl ether in any proportions, acetylacetone is soluble in many organic solvents such as benzene, carbon tetrachloride, chloroform, acetone, and acetic acid.[11] The measured specific conductivity (2.6×10^{-8} mho/cm) is much smaller than the values reported[12] and for AA distilled by the Freiser method,[2] which shows that acetylacetone purified in this study contains less conductive impurities. The relative viscosity coefficient of AA (0.694 cP) is smaller than that of water (0.894 cP). The water content of the purified solvent is approximately 0.01 v/v % as determined both by the Karl Fisher method and by the gas chromatographic standard addition method. Acetylacetone has a convenient liquid

Table I. Physical and Chemical Properties of Acetylacetone

Property	value	ref.
freezing point	−23.2°C	13
boiling point	135~137°C (745 mmHg)	14
density	0.9753 g/cc	15
refractive index	1.4625 (10°C)	3
specific conductance	2.6×10^{-8} mho/cm (25°C)	*
	8.7×10^{-7} mho/cm (25°C)	**
	6.9×10^{-8} mho/cm (25°C)	***
	$0.68\sim2.85\times10^{-6}$ mho/cm	12
dielectric constant	25.7	15
	23 (25°C)	12
viscosity	1.09 cP (0°C)	16
	0.694 cP (25°C)	*
surface tension	32.18 (11°C), 24.14 (81°C) dyn/cm	13
solubility of water	4.1% (25°C)	17
	3.9 g/100 g (25°C)	*
solubility in water	17.2 g/100 ml (20°C)	14
	19.0 g/100 g (25°C)	*
dissociation constant	8.82 (pK, 25°C, 0.1 *M* Cl_4^- aq.)	18
% enol form of AA	81.4	19
water content in AA	0.01%	*

* this work,
** acetylacetone obtained commercially,
*** acetylacetone distilled by the Freiser method.

range, viscosity, and dielectric constant suitable for a non-aqueous polarographic solvent.

Solubilities of Supporting Electrolytes

The solubilities of various electrolytes were measured as follows; the saturated AA solutions of the purified salts were equilibrated for an hour at 40°C and for 2 hours at 25°C. Then the solutions were evaporated and dried to constant weight under reduced pressure. The solubilities thus obtained are presented in Table II. Sodium and potassium chlorides were not soluble more than 0.05 g/100 ml soln., and perchlorates of potassium, rubidium, and tetramethylammonium were also less soluble. The solubilities of perchlorates of lithium, sodium, and tetrabutylammonium are more than 1 *M*, and these salts can be used as supporting electrolytes. In this study, tetrabutylammonium perchlorate was chosen as a supporting electrolyte because the coordinative relaxation reactions of reduced metal acetylacetonates often occur when $LiClO_4$ was used as a supporting electrolyte.[20]

Table II. Solubility of Salts in Acetylacetone at 25°C

Salts	Solubility	
	g/100 ml soln.	(mol/l)
$NaClO_4$	14.2	(1.16)
Et_4NBr	0.56	(0.027)
Bu_4NBr	36.8	(1.14)
Et_4NClO_4	1.48	(0.064)
Pr_4NClO_4	2.72	(0.096)

Accessible Potential Range

Figure 1 shows the DC residual currents in 0.1 *M* TBAP–AA solution at a stationary Pt wire electrode and at DME. As shown in Fig. 1 (c) and (d), large reduction waves of the impurities in the commercial AA are observed in the vicinity of −1.0V,

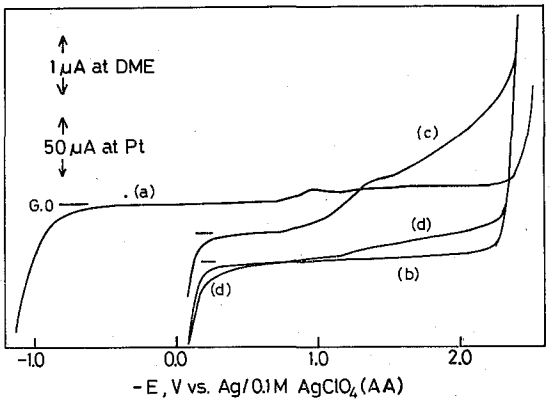

Fig. 1. Background DC polarograms in 0.1 *M* TBAP–acetylacetone solution. (a) at stationary Pt wire electrode, (b) at DME in distilled AA, (c) at DME in commercial AA, (d) at DME in AA distilled by Freiser method.

and the remarkable increase of the residual current is also observed in AA distilled by the Freiser method.[2] In AA purified in this study, the accessible potential ranges are from +0.9 to −2.35 V at Pt, and from −0.2 to −2.25 V at DME, *vs.* Ag/0.1 M $AgClO_4$(AA), respectively. These wide potential ranges verify the applicability of AA as a new electrochemical non-aqueous solvent.

Drop Time - Potential Curve

The drop time - potential curve in pure AA is shown in Fig. 2, which shows no specific adsorption in 0.1 *M* TBAP – AA solution. The electrocapillary maximum was near −0.9 V *vs.* Ag/0.1 *M* $AgClO_4$ (AA). A little depression of the capillary curve was observed in the potential range from −0.9 to −1.5 V in water saturated AA, which corresponds to the case of the solvent extraction.

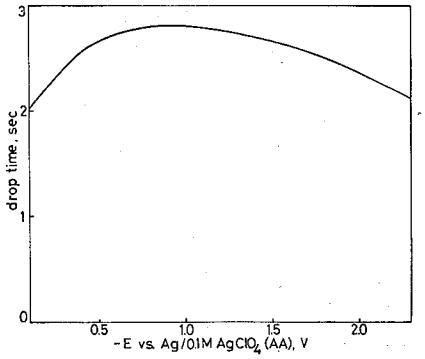

Fig. 2. Drop time – potential curve in 0.1 *M* TBAP – AA solution.

Polarographic Reductions of Metal Acetylacetonates

Polarographic reductions of metal acetylacetonates such as Mn(III), Co(III), Fe(III), Pb(II), Cu(II), Ni(II), and U(VI) in pure AA were studied by DC, current–

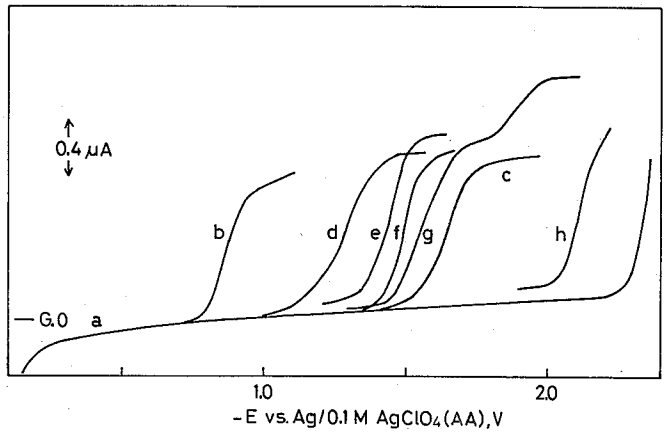

Fig. 3. DC polarograms of metal acetylacetonates in non-aqueous AA. scan rate: 2 mV/sec, 0.4 m*M* M-AA (0.2 m*M* for $CuAA_2$ and $PbAA_2$) in 0.1 *M* TBAP – AA solution, (a) residual current, (b) $MnAA_3$, (c) $PbAA_2$, (d) $CoAA_3$, (e) $FeAA_3$, (f) $CuAA_2$, (g) UO_2AA_2, (h) $NiAA_2$.

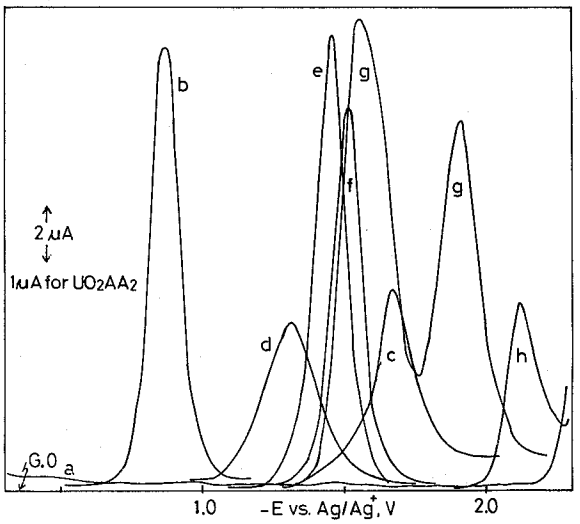

Fig. 4. Differential pulse polarograms of metal acetylacetonates in non-aqueous AA.
scan rate; 2 mV/sec, modulation amplitude; 50 mV, t; 2.0 sec, 0.4 m*M* M-AA (0.2 m*M* for $CuAA_2$) in 0.1 *M* TBAP – AA solution, (a) residual current, (b) $MnAA_3$, (c) $PbAA_2$, (d) $CoAA_3$, (e) $FeAA_3$, (f) $CuAA_2$, (g) UO_2AA_2, (h) $NiAA_2$.

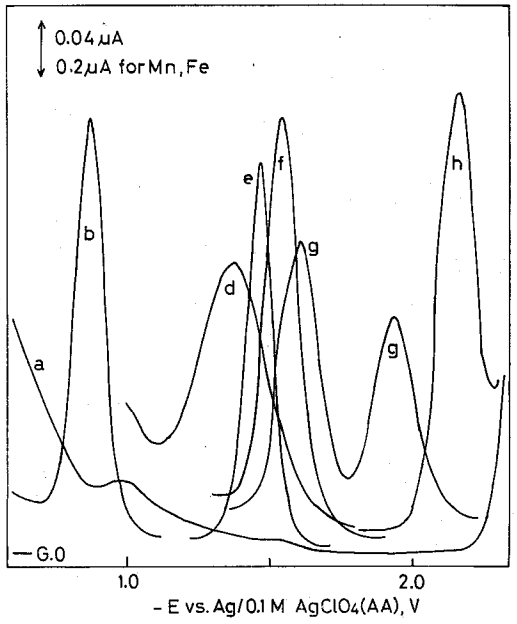

Fig. 5. Phase sensitive AC polarograms of metal acetylacetonates in non-aqueous AA.
scan rate; 2 mV/sec, ΔE; 10 mV, t; 2.0 sec, 0.4 m*M* M-AA (0.2 m*M* for $CuAA_2$) in 0.1 *M* TBAP – AA solution, (a) residual current, (b) $MnAA_3$, (d) $CoAA_3$, (e) $FeAA_3$, (f) $CuAA_2$, (g) UO_2AA_2, (h) $NiAA_2$.

Table III. Summary of Polarographic Reductions of Metal Acetylacetonates in AA (0.4 m*M* M-AA (0.2 m*M* for $CuAA_2$ and $PbAA_2$) in 0.1 *M* TBAP – AA solution at 25°C)

M-AA	DC			SDC		Pulse		DP		AC		PSAC		
	$-E_{1/2}$	I_d	ΔE	$-E_{1/2}$	i	$-E_{1/2}$	i	$-E_p$	i	$-E_p$	i	$-E_p$	i	$W_{1/2}$
Mn (III)	0.867	1.71	59	0.865	2.61	0.875	10.5	0.861	38.0	0.873	2.79	0.873	3.36	112
Pb (II)	1.628	3.92	110	1.616	7.01	1.693	25.2	1.680	32.5	—	—	—	—	—
Co (III)	1.266	2.01	98	1.265	3.45	1.339	11.1	1.309	13.9	N.R.		1.375	0.381	241
Fe (III)	1.433	2.07	74	1.435	3.49	1.455	11.3	1.451	39.7	1.469	3.42	1.467	3.34	113
Cu (II)	1.486	4.08	60	1.480	7.30	1.525	24.7	1.504	65.8	1.556	0.483	1.539	1.39	133
U (VI) 1st	1.552	2.10	111	1.554	3.88	1.545	8.63	1.547	18.2	1.595	0.151	1.605	0.443	165
2nd	1.891	0.797	67	1.869	0.98	1.949	7.78	1.903	12.5	1.961	0.082	1.928	0.309	161
Ni (II)	2.134	1.47	49	2.129	2.44	2.134	11.4	2.114	16.6	2.157	0.491	2.160	0.615	134

$E_{1/2}$ and E_p; half-wave potential and peak potential in V *vs.* Ag/Ag^+, E and $W_{1/2}$; $E_{1/4}-E_{3/4}$ (56.5/n for reversible wave) and half-width (90/n for reversible wave) in mV, I_d; diffusion current constant in A/m*M* $mg^{2/3}S^{-1/2}$, i; i_{meas}/C in μA/m*M*.

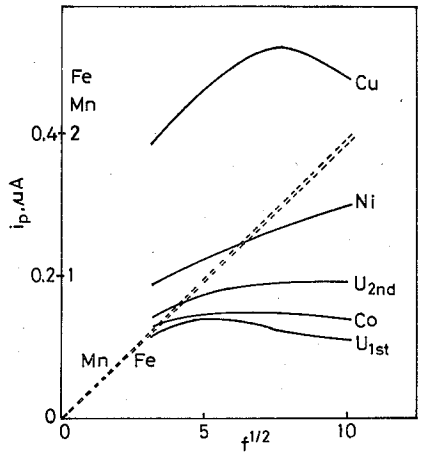

Fig. 6. Variations of PSAC peak currents with frequency. scan rate; 5 mV/sec, ΔE; 10 mV, 0.4 m*M* M-AA in 0.1 *M* TBAP – AA solution.

sampled DC (SDC), pulse (P), differential pulse (DP), Tast AC (AC), and Tast phase sensitive AC (PSAC) polarographies. The typical polarograms are shown in Figs. 3～5 for DC, DP, and PSAC polarographies, respectively, and the polarographic data are summarized in Table III. Figure 6 shows the dependence of PSAC polarographic peak current on the frequencies of superimposed AC.[21]

Acetylacetonates of manganse(III), cobalt(III), and iron(III) exhibit the diffusion-controlled waves of one-electron reduction, and those of copper(II) and nickel (II) give the diffusion-controlled and two-electron reduction waves. The reduction wave of lead(II) acetylacetonate is slightly kinetic and two-electron one. Uranyl acetylacetonate is reduced by two steps: both are one-electron reduction waves, of which the first is diffusion-controlled and the second is kinetic. In the first

reduction step, U(VI) is reduced to U(V), and the second wave from U(V) to U(IV) exhibits apparently more reversibility. The limiting current of the second wave is smaller than that of the first, and not only the first wave but also the second one decreases when UO_2AA_2 is electrolyzed at the constant potential of -1.7 V. These results are attributed to the disproportionation reaction of U(V) to U(VI) and U (IV) which occurs after the first reduction step: $2U(V) \rightarrow U(VI) + U(IV)$. When UO_2AA_2 is completely electrolyzed at -2.1 V, only one well-defined anodic wave is observed at a more positive potentials than that of the first wave. Diffusion currents of DC polarograms are proportional to the concentration of metal acetylacetonates in the range of 10^{-5} to 10^{-3} *M*. As for UO_2AA_2, the ratio of the height of the second wave to that of the first becomes smaller with decrease of the concentration of this chelate. DC polarograms of $FeAA_3$ and $CuAA_2$ show polarographic maxima at the concentration more than 10^{-3} and 2.0×10^{-4} *M*, respectively.

As shown in Table III and Fig. 6, the PSAC polarographic reduction process of $MnAA_3$ and $FeAA_3$ are closely reversible because their peak currents are proportional to a square root of AC frequencies and values of their half-width are nearly equal to 90 mV. The reversibility order of metal acetylacetonates are considered as follows: $Mn(III) > U_{2nd} > Fe(III) > Co(III) \sim Ni(II) > U_{1st} > Cu(II) > Pb(II)$ for DC, and $Mn(III) \sim Fe(III) > U_{2nd} \sim U_{1st} > Co(III) > Cu(II) > Ni(II)$ for PSAC polarography.

Acetylacetonates of other metal ions such as Be(II), Mg(II), Ca(II), Al(III),

Table IV. Effect of Concentration of TBAP on DC, SDC, and Pulse Polarographic Reductions of $MnAA_3$ and $FeAA_3$ in AA (0.4 m*M* $MnAA_3$ and $FeAA_3$ in TBAP – AA solution)

TBAP Concn. (*M*)	Parameter	DC		SDC		Pulse	
		$MnAA_3$	$FeAA_3$	$MnAA_3$	$FeAA_3$	$MnAA_3$	$FeAA_3$
0.025	$-E_{1/2}$	0.878	1.420	0.889	1.419	0.894	1.448
	i	2.29	2.34	2.78	2.88	10.9	10.5
	ΔE	60	71				
0.05	$-E_{1/2}$	0.873	1.426	0.883	1.415	0.871	1.447
	i	2.21	2.44	2.68	3.18	10.7	11.1
	ΔE	58	77				
0.10	$-E_{1/2}$	0.867	1.433	0.865	1.435	0.875	1.455
	i	2.19	2.66	2.61	3.49	10.5	11.3
	ΔE	59	74				
0.15	$-E_{1/2}$	0.849	1.439	0.859	1.426	0.877	1.446
	i	2.09	2.63	2.53	3.45	9.88	12.3
	ΔE	59	76				
0.20	$-E_{1/2}$	0.856	1.450	0.851	1.438	0.901	1.473
	i	1.80	2.56	1.44	3.25	8.58	12.3
	ΔE	60	74				

ΔE; $E_{1/4} - E_{3/4}$ (mV), $E_{1/2}$: half-wave potential (V *vs.* Ag/Ag^+), i: i_{meas}/C ($\mu A/mM$)

Ga(III), In(III), Zn(II), Sc(III), La(III), Zr(IV), V(V), Cr(III), and Co(II) do not show polarographic waves in 0.1 *M* TBAP – AA solution. Acetylacetonates of Li(I), Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), Ti(IV), and Th(VI) are not dissolved up to 4.0×10^{-4} *M*, and their saturated solutions give no reduction wave. Acetylacetonates of Cd(II), Tl(I), Fe(II), and Mn(II) are not dissolved up to 4.0×10^{-4} *M*, either, but $CdAA_2$ shows ill-defined wave and TlAA well-defined one, respectively. The solubility of $FeAA_2$ and $MnAA_2$ increases with time, and the polarograms of the resulting solutions are identical with those of $FeAA_3$ and $MnAA_3$.

Effect of Concentration of Supporting Electrolyte on Polarographic Reductions

The effect of the concentration of Bu_4NClO_4 as a supporting electrolyte on the polarographic reductions of various metal acetylacetonates has been studied, and above all, the polarographic behavior of $MnAA_3$ and $FeAA_3$ are presented in Tables IV and V on behalf of the reversible reduction processes.

The polarographic diffusion current is proportional to a square root of the diffusion coefficient of electroactive species. The modified Ilkovic equation (1) shows that the diffusion current, i_d, decreases with increase of the concentration of supporting electrolyte, C_s,

$$i_d=607\cdot n\cdot D_o^{1/2}\cdot C\cdot m^{2/3}\cdot t^{1/6}(1-B\cdot D_o^{-1}\cdot C_s^{1/2}/2) \quad (1)$$

where B is a constant, D_o the diffusion coefficient at infinite dilution, and others have their usual meanings. The practical relation, however, deviates from Eq. (1) as

Table V. Effect of Concentration of TBAP on DP, AC, and PSAC Polarographic Reductions of $MnAA_3$ and $FeAA_3$ in AA (0.4 m*M* $MnAA_3$ and $FeAA_3$ in TBAP – AA solution)

TBAP Concn. (*M*)	Parameter	DP		AC		PSAC	
		$MnAA_3$	$FeAA_3$	$MnAA_3$	$FeAA_3$	$MnAA_3$	$FeAA_3$
0.025	$-E_p$	0.879	1.436	0.888	1.459	0.886	1.454
	i	39.5	35.8	2.06	3.35	2.85	2.17
	$W_{1/2}$					116	113
0.05	$-E_p$	0.865	1.444	0.877	1.468	0.880	1.452
	i	38.0	37.5	1.83	2.88	3.38	2.70
	$W_{1/2}$					112	112
0.10	$-E_p$	0.861	1.451	0.873	1.469	0.873	1.467
	i	38.0	39.7	2.79	3.42	3.36	3.34
	$W_{1/2}$					112	113
0.15	$-E_p$	0.857	1.439	0.864	1.481	0.863	1.476
	i	34.0	42.5	2.68	3.33	3.43	3.45
	$W_{1/2}$					104	120
0.20	$-E_p$	0.852	1.469	0.864	1.508	0.862	1.499
	i	31.3	42.5	2.60	3.05	3.65	3.28
	$W_{1/2}$					108	133

E_p: peak potential (V *vs.* Ag/Ag^+), $W_{1/2}$: half-width (mV), i: i_{meas}/C (μA/m*M*)

Table VI. Relative Viscosity of TBAP – AA Solution at 25°C

Concn. of TBAP (M)	0	0.025	0.050	0.100	0.150	0.200
Viscosity (cP)	0.694	0.707	0.744	0.747	0.810	0.835

follows[22]): (1) conformable type to theoretical Onsager equation,[23] (2) upwards convex type, and (3) S-shaped type, of dependence of diffusion current on concentration. The diffusion currents are also in inverse proportion to a square root of relative viscosities, η, of solutions according to the Ilkovic-Stokes-Einstein equation (2),

$$i_d = K \cdot \eta^{1/2} \tag{2}$$

where K is a constant. Table VI shows the measured viscosity coefficients at the various concentrations of a supporting electrolyte TBAP in AA. In polarographies, the diffusion coefficients are determined most exactly by pulse polarography[24,25] which eliminates a depletion effect. The pulse polarographic currents are nearly proportional to a square root of diffusion coefficients, and so the ratio of the measured currents is proportional to that of a square root of the diffusion coefficients in each solution.

According to Eqs. (1) and (2), and type (1), the higher the concentration of TBAP, the smaller the DC, SDC, P, and DP polarographic currents for $MnAA_3$, as presented in Tables IV and V. As for $FeAA_3$, it is seen that these polarographic currents change according to type (2). From the values of ΔE in Table IV, it is concluded that the concentration of supporting electrolyte, 0.05 M, is sufficient for DC and SDC polarography, and 0.025 M for P and DP polarographies.[26] AC polarographic currents change upwards convexly with increase of the concentration of TBAP, and the maxima are considered to be near at 0.1 M. In PSAC polarography, the higher the concentration of TBAP, the higher the peak currents of $MnAA_3$ and $FeAA_3$, which may be attributed to the decrease of the effect of ohmic iR drop. The concentration of supporting electrolyte in AC and PSAC polarography should be 0.1 M or more, because the reduction processes incline generally to be more reversible with increase of the concentration of supporting electrolyte.

Comparison of the Various Polarographic Currents

Table VII shows the ratios of SDC, P, DP, AC, and PSAC polarographic currents to the average diffusion current in DC polarography (i_{DC}) of metal acetylacetonates in 0.1 M TBAP - AA solution. The theoretical value of i_{SDC}/i_{DC} is ca. 7/6 because i_{SDC} is nearly equal to the maximum faradic current during a drop life in DC polarography given by the Ilkovic equation (3).

$$i_{max} = 708 \cdot n \cdot D^{1/2} \cdot C \cdot m^{2/3} \cdot t^{1/6} = (708/607) \cdot i_{DC} \tag{3}$$

In practice, as shown in Table VII, the values of i_{SDC}/i_{DC} were somewhat greater than the theoretical value of 7/6 for most cases except $U(VI)_{2nd}$ whose process is kinetic. The sensitivity of the pulse polarography with respect to DC polarography, i_P/i_{DC}, can readily be calculated by Eqs. (4), (5), and (6).

$$i_p = 462 \cdot n \cdot D^{1/2} \cdot C \cdot m^{2/3} \cdot t^{2/3} \cdot t_m^{-1/2} \tag{4}$$

$$t_m = \tau - \delta_t/2 \tag{5}$$

$$i_P/i_{DC} = (462/607)(t/t_m)^{1/2} \tag{6}$$

Table VII. Ratios of Various Polarographic Reduction Currents (0.4 m*M* M-AA (0.2 m*M* for $CuAA_2$) in 0.1 *M* TBAP – AA solution)

M-AA	i_{SDC}/i_{DC}	i_P/i_{DC}	i_{DP}/i_{DC}	i_{AC}/i_{CD}	i_{PSAC}/i_{DC}	i_{PSAC}/i_{AC}
Mn (III)	1.19	4.79	17.4	1.27	1.54	1.21
Co (III)	1.34	4.31	5.43	—	0.148	—
Fe (III)	1.31	4.25	14.9	1.29	1.26	0.977
Cu (II)	1.40	4.72	12.6	0.0923	0.267	2.89
U (VI) 1st	1.44	3.20	6.76	0.0561	0.164	2.92
2nd	0.961	7.62	12.3	0.0804	0.303	3.77
Ni (II)	1.29	6.04	8.78	0.261	0.326	1.25

where, i_P is the normal pulse polarographic current on the diffusion plateau, τ the pulse width, and δ_t the sample width. The ratios of i_P/i_{DC} for the diffusion current of metal acetylacetonates are almost comparable to the theoretical value of 4.88 calculated by Eq. (6) under the experimental conditions of t=2.0 sec, τ=57 m sec, and δ_t=16.7 m sec. Of all the current ratios, the values of i_{DP}/i_{DC} are largest and in the ranges of 5.4~17.4, which indicate the potentiality of the differential pulse polarography for the trace analysis. The values of i_{AC}/i_{DC}, i_{PSAC}/i_{DC}, and i_{PSAC}/i_{AC} for $MnAA_3$ and $FeAA_3$ do not much deviate from unity, reflecting the reversible electrode process of these acetylacetonates.

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